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## SPECIFICATION

### TITLE OF THE INVENTION

X-RAY MASK BLANK AND X-RAY MASK

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### REFERENCE TO RELATED APPLICATION

This application claims the priority right under 35 U.S.C 119, of Japanese Patent Application No. Hei 09-80762 filed on March 31, 1997, the entire disclosure of which is incorporated herein by reference.

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention:

The present invention relates to an x-ray mask for use in an x-ray lithography method and an x-ray mask blank which is ~~a~~ <sup>part</sup> material of the x-ray mask.

#### 2. Description of the Related Art:

In <sup>the</sup> ~~a~~ semiconductor industry, ~~as~~ <sup>the</sup> ~~a~~ technique <sup>of</sup> ~~for~~ forming an integrated circuit constituted of a fine pattern on a silicon substrate or the like, <sup>using</sup> ~~a~~ photolithography method for transferring the fine pattern by the use of a visible light and an ultraviolet light as an exposing electromagnetic wave, is well known. However, a recent advance in ~~a~~ semiconductor technique greatly promotes <sup>the</sup> ~~a~~ high integration of a semiconductor device such as <sup>as</sup> ~~a~~ VLSI, <sup>and this</sup> ~~and this~~ results in a requirement for the technique for transferring the

A fine pattern with high accuracy beyond the transfer limit (a principled limit due to wavelength) of the visible light and the ultraviolet light for use in the conventional photolithography method. In order to transfer such a fine pattern, an x-ray lithography method, using an x-ray whose wavelength is shorter than the wavelength of the visible light and the ultraviolet light, is attempted.

Fig. 1 is a cross sectional view showing a structure of an x-ray mask for use in the x-ray lithography. Fig. 2 is a cross sectional view showing the structure of an example of an x-ray mask blank as an intermediate product obtained in an intermediate process during manufacturing the x-ray mask.

As shown in Fig. 1, an x-ray mask 1 comprises an x-ray membrane 12 for transmitting the x-ray and an x-ray absorbing film pattern 13a formed on the x-ray membrane 12. The x-ray membrane 12 is supported by a silicon frame body 11a which is formed by removing <sup>a</sup> ~~the other~~ portion so that the periphery alone of the silicon substrate may remain. When this x-ray mask 1 is manufactured, the x-ray mask blank ~~to be the~~ intermediate product is manufactured in the intermediate <sup>step</sup> ~~process~~. This x-ray mask blank is further processed, so that the x-ray mask is obtained. In this industry, <sup>while</sup> ~~although, of course,~~ the x-ray mask which is a finished product <sup>which</sup> ~~is to be dealt in~~ the x-ray mask blank, which is the intermediate product, is also often ~~to be~~ independently dealt ~~in~~.

As shown in Fig. 2, an x-ray mask blank 2 comprises the x-ray membrane 12 formed on a silicon substrate 11 and an x-ray absorbing film 13 formed on the x-ray membrane. <sup>12</sup>  
A

Silicon nitride, silicon carbide, diamond or the like is  
5 A generally used as the x-ray membrane 12. An amorphous material,  
A including tantalum (Ta), having an excellent resistance to x-ray  
A radiation, is often used as the x-ray absorbing film 13.

A *One example of a*  
A ~~For the process of manufacturing the x-ray mask 1 from the~~  
A ~~x-ray mask blank 2, for example, the following method is used.~~  
10 A ~~That is, a~~ resist film on which a desired pattern is formed is  
arranged on the x-ray mask blank 2 shown in Fig. 2. This pattern  
is then used as a mask so as to perform a dry etching, so that  
the x-ray absorbing film pattern is formed. After that, a center  
A area, formed on a rear surface and to be a window area of the x-  
15 A ray membrane 12, is removed by a reactive ion etching (RIE) using  
4-fluorocarbon (CF<sub>4</sub>) as etching gas. The remaining film (12a: see  
A Fig. 1) is then used as the mask ~~so as~~ to etch the silicon  
A substrate 11 ~~by~~ *using* an etching liquid constituted of a mixed liquid  
A of fluoric acid and nitric acid, *and* whereby the x-ray mask 1 (see  
20 Fig. 1) is obtained. In this case, an electron beam (EB) resist  
is generally used as the resist, and the pattern is formed by  
means of an EB lithography.

For the x-ray membrane 12, a high transmittance to the x-ray, a high Young's modulus of elasticity, a proper tensile  
25 stress, a resistance to x-ray radiation, the high transmittance

1 A within a visible light range, and the like are required. <sup>These</sup> ~~A~~ The characteristics will be described below. The transmittance to the x-ray is required during an exposure. The higher the <sup>the</sup> transmittance is, the shorter ~~A~~ <sup>the</sup> time required for the exposure  
5 A ~~can~~ become. This is effective for improving throughput. The A Young's modulus of elasticity has an influence on ~~A~~ strength of A the film and ~~A~~ deformation of an absorber pattern. The higher the Young's modulus of elasticity is, the higher the film strength A becomes. This is effective for suppressing misalignment. The 10 A proper tensile stress is needed <sup>so</sup> ~~in order~~ that the film is self-supported. Since the x-ray membrane is irradiated with the x-ray A during the exposure, it is necessary <sup>to not have</sup> ~~A~~ <sup>to cause no</sup> damage due to this x-ray radiation, and thus the resistance to x-ray radiation is required. Since an alignment of the mask attached to an x-ray 15 stepper and a wafer is accomplished by the use of a light source A within the visible light range, ~~the~~ high transmittance to an alignment light source (the visible light) is needed in order to A achieve a highly accurate alignment. Furthermore, <sup>the</sup> ~~A~~ film surface is required to be smooth. <sup>Surface</sup> ~~A~~ <sup>surface</sup> smoothness is needed for A highly accurate pattern formation on the absorber.  
20

In order to satisfy these requirements, various materials and manufacturing methods have been studied. Since it is A confirmed that the silicon carbide <sup>has</sup> ~~A~~ causes no damage due to the x-ray in the silicon nitride, the silicon carbide (SiC) and the 25 diamond which have been heretofore used as the x-ray membrane, it

may safely be said that the silicon carbide is the most promising material. However, since the SiC film ~~for the general use~~ has a polycrystalline structure, ~~the SiC film~~ has the film surface which is rougher than 6 nm (Ra: a center-line average roughness) due to a crystalline structure. For ~~smoothing of~~ <sup>Smooth</sup> the surface of this SiC film, an etch back method and a mechanical polishing method are carried out after the film formation. ~~The~~ <sup>In</sup> etch back method, ~~is the technique in which~~ the rough SiC film is coated with the resist, and the thus obtained smooth resist surface is transferred onto ~~the~~ SiC film by the dry etching. ~~The~~ <sup>FOR</sup> mechanical polishing, ~~is the method in which~~ a hard grain such as the diamond and alumina is used as an abrasive material so as to physically grind ~~an~~ unevenness on the surface of the SiC film. For example, according to Japanese Patent Publication No. 7-75219, ~~the~~ <sup>a</sup> surface roughness of 20 nm or less is obtained by the etch back and the mechanical polishing. Although ~~a~~ <sup>the</sup> definition of the surface roughness is not clear in this publication, this roughness is expected to be a maximum height (Rmax) and corresponds to about 2 nm or less in terms of Ra.

Recently, due to the advance in ~~the~~ photolithography technique, ~~an~~ introduction of the x-ray lithography has been performed later. At present, ~~the~~ introduction from a generation of 1G bit-DRAM (design rule: 0.18  $\mu$ m) is anticipated. Even if the x-ray lithography is introduced from 1G, the x-ray lithography is characterized by <sup>in</sup> that it can be used through a plurality of 20(26/99)

generations up to 4G, 16G and 64G. Assuming that the x-ray  
A lithography is used for 64G, ~~the~~ position precision required for  
A the x-ray mask becomes severer, and ~~thus the position precision~~  
is required to be as high as 10 nm. The inventor has already  
5 A found that, in order to suppress ~~to~~ such a position precision, it  
is effective to equalize an internal stress in an area in which a  
mask pattern is formed on the x-ray absorbing film (Japanese  
Patent Application No. 8-233402). As a result of a further study,  
the inventor has found that the surface roughness of the x-ray  
10 membrane has a sensitive influence on a stress distribution of  
the x-ray absorbing film formed on the x-ray membrane.

#### SUMMARY OF THE INVENTION

It is therefore an object of the present invention to  
15 A provide an x-ray mask blank, in which a stress distribution of an  
A x-ray absorbing film is suppressed, and an x-ray mask capable of a  
highly precise pattern transfer.

A In accordance with the first aspect of the present  
invention, there is provided an x-ray mask blank having at  
20 least an x-ray membrane on a substrate, wherein the x-ray  
membrane has a surface condition satisfying the following  
expression (1):

$$(Ra_{\max} - Ra_{\min}) / (Ra_{\max} + Ra_{\min}) \leq 0.15 \quad (1)$$

where  $Ra_{\max}$  denotes a maximum value of Ra of a surface  
25 roughness (Ra: center-line average roughness) on a plurality of

points within a predetermined area on the x-ray membrane, and  $R_{a_{min}}$  denotes a minimum value of  $R_a$  of the surface roughness ( $R_a$ : center-line average roughness) on a plurality of points within a predetermined area on the x-ray membrane.

5 A In accordance with ~~the~~<sup>a</sup> second aspect of the present invention, there is provided an x-ray mask blank according to the first aspect, wherein an average of the surface roughness ( $R_a$ : center-line average roughness) ~~on~~<sup>of</sup> a plurality of points within a predetermined area on the x-ray membrane is 1.0 nm or less.

10 A In accordance with ~~the~~<sup>a</sup> third aspect of the present invention, there is provided an x-ray mask blank according to the first or second aspect, wherein the surface of the x-ray membrane is a generally uniformly polished surface.

15 A In accordance with ~~the~~<sup>a</sup> fourth aspect of the present invention, there is provided an x-ray mask blank according to any one of the first through third aspects, wherein the x-ray membrane comprises a silicon carbide film.

20 A In accordance with ~~the~~<sup>a</sup> fifth aspect of the present invention, there is provided an x-ray mask having an x-ray absorbing film pattern on an x-ray membrane supported by a frame body, wherein the x-ray mask is manufactured by the use of the x-ray mask blank according to any one of the first through fourth aspects.

25 The inventor has studied the surface roughness of the x-ray membrane and the stress distribution of the x-ray absorbing film.

As a result, it is found that the distribution of the surface roughness of the x-ray membrane would cause the stress distribution of the absorbing film, and thus ~~the~~ pattern position precision is deteriorated. The condition of the distribution of the surface roughness can be represented by the value of the left side of the expression (1). Now, assuming that the value of the left side of the expression (1) is defined as the value of the distribution of the surface roughness, if the value of the distribution of the surface roughness of the x-ray membrane exceeds 0.15 (15%), the stress distribution of the x-ray absorbing film is increased, which may deteriorate the pattern position precision. Therefore, Preferably, the value of the distribution of the surface roughness of the x-ray membrane is 0.15 or less. More preferably, the value is 0.1 or less.

Since it is important for the x-ray absorbing film to control the stress distribution within the area in which a mask pattern is formed, it is preferable to similarly control the distribution of the surface roughness of the x-ray membrane within the area in which the mask pattern is formed. Furthermore, the average of the surface roughness (Ra: center-line average roughness) on a plurality of points within a predetermined area on the x-ray membrane is 1.0 nm or less, whereby so that it is possible to suppress the distribution of the surface roughness of the x-ray membrane to some extent.

A silicon substrate or the like is ~~herein~~ used as the

substrate. SiC, SiN, diamond or the like is used as the x-ray

A <sup>Preferably</sup> membrane. <sup>More specifically,</sup> <sup>preferably,</sup> SiC is used in view of <sup>HS</sup> a resistance to x-ray radiation.

A Moreover, in order to suppress <sup>1</sup> variation in the surface

5 roughness of the x-ray membrane, it is effective to uniformly polish the substrate having the x-ray membrane. For this purpose,

the substrate having the x-ray membrane is affixed to a substrate

A <sup>a</sup> fixing jig, and a load to polishing means, such as an abrasive

A cloth, is applied to <sup>uniformly</sup> the substrate fixing jig so as to polish the

10 A substrate, whereby the substrate can be uniformly polished.

Preferably, a method of affixing the substrate having the x-ray membrane to the substrate fixing jig is the method of affixing the substrate to an SUS jig through water (a water affixing

A <sup>Methods</sup> method). That is, the method of affixing the substrate to the

15 substrate fixing jig by the use of a wax, an adhesive tape or the like is not preferable, because the relatively thin substrate

A such as the x-ray mask blank is prone to a deformation <sup>while</sup> during

A being affixed and thus the variation <sup>1</sup> in polishing is caused when

the substrate is polished. On the other hand, if the substrate is

20 affixed to the substrate fixing jig by the use of the water affixing method, the deformation of the substrate can be avoided

A when the substrate is affixed, and thus the uniform polishing is possible. More specifically, when SiC is used as the x-ray

A membrane, it is preferable to apply <sup>a</sup> the load of about 50-400 g/cm<sup>2</sup>.

25 A Since SiC is <sup>a</sup> hard film, it is preferable that the <sup>diamond</sup> is <sup>diamonds</sup>

used as an abrasive material. It should be noted that a method as described below is used in order to prevent a scratch from being made on the surface. That is, the surface is polished by the use of the <sup>a</sup> diamond whose average particle diameter is as relatively small as about 0.05-0.3  $\mu\text{m}$  or the <sup>a</sup> diamond whose average particle diameter is larger than the former (about 0.3-0.6  $\mu\text{m}$ ), and then the surface is polished by the use of colloidal silica. Moreover, when the <sup>a</sup> colloidal silica is used without the use of the diamond, hydrogen peroxide is contained in the colloidal silica, whereby it is possible to obtain the <sup>a</sup> surface which is flat and is not scratched.

The x-ray mask blank of the present invention may be the one in which the film <sup>is</sup> constituted by an etching stop layer, an adhesive layer, a reflection preventing layer and a conductive layer is disposed between the x-ray membrane and the x-ray absorbing film. Alternatively, the x-ray mask blank may be also the one in which a mask layer, a protective layer and a conductive layer are disposed on the x-ray absorbing film.

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#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a cross sectional view for describing a structure of an x-ray mask;

Fig. 2 is a cross sectional view for describing the structure of an x-ray mask blank;

25 Fig. 3 is an illustration of a method of manufacturing the

x-ray mask according to embodiments of the present invention; and

Fig. 4 is a table generally showing a distribution value of a surface roughness of an x-ray membrane, an average of the surface roughness of the x-ray membrane, a stress distribution of 5 an x-ray absorbing film and a position precision of an x-ray absorbing film pattern of the embodiments and a comparison example.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

10 An x-ray mask blank and an x-ray mask of embodiments will  
be described with reference to Fig. 3.

[Embodiment 1]

[Formation of x-ray membrane]

A <sup>First</sup> ~~In the first place,~~ a silicon carbide film is formed as an 15 x-ray membrane 12 on both the surfaces of a silicon substrate 11. The silicon substrate of 4 in.  $\phi$  in size, of 2 mm in thickness and of a crystalline orientation of (100) is used as the silicon substrate 11. The silicon carbide film as the x-ray membrane is also formed to 2.1  $\mu\text{m}$  in thickness by a CVD process by the use of 20 dichlorosilane and acetylene. Next, the surface of the x-ray membrane 12 is smoothed by a mechanical polishing. The mechanical polishing is performed in the following manner. First, the rear surface of the substrate on which the x-ray membrane 12 is formed is affixed to a stainless (SUS) jig by a water affixing method, 25 and the film surface is brought into contact with a solidifying

*of the present invention*

polymer type soft abrasive cloth in which a diamond particle of an average particle diameter of  $1/8 \mu\text{m}$  (0.05-0.35  $\mu\text{m}$  in diameter: Nihon Engis) is dispersed. Then, a load of  $200 \text{ g/cm}^2$  is applied to the jig while the jig is rotated at 60 rpm, whereby the 5 surface is polished for five minutes.

A A surface roughness ( $\text{Ra}$ ) <sup>of</sup> <sub>on</sub> 100 points within a range of 30  $\times 30 \text{ mm}$  <sup>at</sup> <sub>at</sub> the center of the substrate on the thus obtained surface is measured by an atomic force microscope, and a value (a distribution value of the surface roughness) of the left side of 10 A an expression (1) is determined from a maximum value of  $\text{Ra}$  and a <sup>Resulting</sup> <sub>minimum</sub> value of  $\text{Ra}$ . The resultant value is 0.05, and the average of the surface roughness is 0.35 nm. At this time, a scratch on the surface is  $0.2 \mu\text{m}$  or less.

[Formation of x-ray absorbing film]

15 Next, as shown in Fig. 3(B), an x-ray absorbing film 13 of tantalum and boron is formed to  $0.5 \mu\text{m}$  in thickness on the x-ray membrane 12 by a DC magnetron sputtering process. A sintered body containing tantalum and boron in an atomicity ratio (Ta/B) of 8 A to 2 is used as a sputter target. <sup>The sputter</sup> <sub>gas</sub> is  $\text{Xe}$ , an RF power 20 A density is set at  $6.5 \text{ W/cm}^2$  and a sputter gas pressure is set at 0.35 Pa. Next, this substrate is annealed at  $250^\circ\text{C}$  for two hours A in a nitrogen atmosphere ~~so as~~ to thereby obtain the x-ray absorbing film 13 of a low stress of 10 MPa or less. At this time, A a stress <sup>having</sup> <sub>of</sub> the x-ray absorbing film is measured by a highly

A precise stress measuring unit (WS-5000: NTT Advance Technology) and is within the same range as the above-described range in which the surface roughness of the x-ray membrane is measured. As a result, the stress is  $0 \pm 4$  MPa.

5 [Formation of etching mask layer]

Next, as shown in Fig. 3(C), a chromium film containing chromium carbide is formed as an etching mask layer 14 on the x-ray absorbing film 13 by an RF magnetron sputtering process so that it <sup>is</sup> ~~may be~~ 0.05  $\mu\text{m}$  in thickness. Cr is used as the sputter target, the sputter gas <sup>has</sup> ~~is the gas in which~~ 7% of methane ~~is~~ mixed into Ar, the RF power density is set at 6.5 W/cm<sup>2</sup> and the sputter gas pressure is set at 1.2 Pa, thereby obtaining the etching mask layer <sup>An</sup> ~~having a~~ <sup>1</sup> ~~is then obtained~~ of the low stress of 100 MPa or less. The product obtained in this step is also <sup>used</sup> ~~dealt~~ as one type of the x-ray mask blank.

15 [Formation of x-ray absorbing film pattern and Formation of frame body]

A resist film on which a desired pattern is formed is arranged on an x-ray mask blank 2. This pattern is used as the mask so as to perform a dry etching, whereby the x-ray absorbing film pattern is formed. Then, a center area, formed on the rear surface and to be a window area of the x-ray membrane 12, is removed by a reactive ion etching (RIE) <sup>using</sup> ~~by the use of~~ CF<sub>4</sub> as the etching gas. The remaining film 12a is then used as the mask so as to etch the silicon substrate 11 <sup>using</sup> ~~by~~ an etching liquid constituted

of a mixed liquid of fluoric acid and nitric acid, whereby an x-ray silicon frame body 11a is formed, and the x-ray mask is thus obtained. In this case, an electron beam (EB) resist is generally used as the resist, and the pattern is formed by means of an EB 5 lithography.

A misalignment of the x-ray absorbing film pattern (an actual shift of the pattern with respect to a design pattern) of the x-ray mask manufactured by this embodiment is evaluated by a A coordinate measuring device. As a result, <sup>the</sup> <sub>1</sub> position precision is 10 A <sub>1</sub> 18 nm <sup>which is</sup> <sub>1</sub> sufficient.

[Embodiment 2]

[Formation of x-ray membrane]

A <sup>FIRST</sup> In the first place, <sub>1</sub> the silicon carbide film is formed as A the x-ray membrane 12 on both ~~the~~ <sub>1</sub> surfaces of the silicon 15 A substrate 11. The silicon substrate of 4 in.  $\phi$  in size, of 2 mm <sup>A</sup> in thickness and of the crystalline orientation of (100) is used as the silicon substrate 11. The silicon carbide film as the x-ray membrane is also formed to 2.1  $\mu\text{m}$  in thickness by the CVD process by the use of dichlorosilane and acetylene. Next, the 20 surface of the x-ray membrane 12 is smoothed by the mechanical polishing. The mechanical polishing is performed in the following manner. First, the rear surface of the substrate on which the x-ray membrane 12 is formed is affixed to the stainless (SUS) jig, and the film surface is brought into contact with the solidifying A 25 polymer type soft abrasive cloth in which the diamond <sup>a</sup> <sub>1</sub> <sup>particles</sup> <sub>1</sub> particle of

A <sup>An</sup> average particle diameter of  $1/4 \mu\text{m}$  ( $0.1\text{-}0.6 \mu\text{m}$  in diameter:  $\alpha$ ) is dispersed. Then, the load of  $200 \text{ g/cm}^2$  is applied to the jig while the jig is rotated at  $60 \text{ rpm}$ , whereby the surface is polished for five minutes, so that the surface of the surface roughness of  $1 \text{ nm}$  or less in terms of  $\text{Ra}$  is obtained. <sup>The</sup>

A However, the scratch of  $0.2 \mu\text{m}$  or more is on the surface of the thus obtained film. Therefore, moreover, the rear surface of the substrate is fixed to the SUS jig, and the substrate is brought into contact with a suede type (nonwoven fabric type) abrasive cloth in which colloidal silica (its particle diameter:  $60\text{-}80 \text{ nm}$ ) is dispersed. Then, the load of  $180 \text{ g/cm}^2$  is applied to the jig while the jig is rotated at  $60 \text{ rpm}$ , whereby the surface is polished for five minutes, so that the scratch is reduced to  $0.2 \mu\text{m}$  or less on the surface. <sup>The</sup> When the distribution of the surface roughness of the thus obtained x-ray membrane is determined in the same manner as <sup>for</sup> the first embodiment, the distribution is  $0.08$  and the average of the surface roughness is  $0.70 \text{ nm}$ . The thus obtained product is also <sup>Used</sup> dealt as one type of <sup>The</sup> x-ray mask blank.

## 20 [Formation of x-ray absorbing film]

Next, as shown in Fig. 3(B), the x-ray absorbing film 13 of tantalum and boron is formed to  $0.5\text{ }\mu\text{m}$  in thickness on the x-ray membrane 12 by the DC magnetron sputtering process. The sintered body containing tantalum and boron in the atomicity ratio (Ta/B) of 8 to 2 is used as the sputter target. The sputter gas is Xe,

the RF power density is set at  $6.5 \text{ W/cm}^2$ , and the sputter gas pressure is set at 0.35 Pa. Next, this substrate is annealed at  $250^\circ\text{C}$  for two hours in the nitrogen atmosphere so as to thereby obtain the x-ray absorbing film 13 of ~~the~~<sup>a</sup> low stress of 10 MPa or less. When ~~the~~<sup>The</sup> stress distribution on the surface of this film is determined in the same manner as described above, ~~the~~<sup>a</sup> stress distribution is  $0 \pm 5 \text{ MPa}$ . The product obtained in this step is also dealt as one type of ~~the~~<sup>and has a</sup> x-ray mask blank.

[Formation of etching mask layer]

Next, as shown in Fig. 3(C), the chromium film containing chromium carbide is formed as the etching mask layer 14 on the x-ray absorbing film 13 by ~~the~~<sup>a</sup> RF magnetron sputtering process so that it may be  $0.05 \mu\text{m}$  in thickness. Cr is used as the sputter target, the sputter gas ~~is the gas in which~~<sup>has</sup> 7% of methane is mixed into Ar, the RF power density is set at  $6.5 \text{ W/cm}^2$ , and the sputter gas pressure is set at 1.2 Pa, thereby obtaining the etching mask layer of the low stress of 100 MPa or less. The product obtained in this step is also dealt as one type of the x-ray mask blank.

[Formation of x-ray absorbing film pattern and Formation of frame body]

The resist film on which a desired pattern is formed is arranged on the x-ray mask blank 2. This pattern is used as the mask so as to perform the dry etching, whereby the x-ray absorbing film pattern is formed. Then, the center area formed on

10 <sup>A</sup> the rear surface, and to be the window area of the x-ray membrane <sup>using</sup>  
<sup>A</sup> 12 is removed by the reactive ion etching (RIE) <sup>by the use of 4-</sup> carbonfluoride ( $CF_4$ ) as the etching gas. The remaining film 12a  
<sup>A</sup> is then used as the mask ~~so as~~ to etch the silicon substrate 11  
5 <sup>A</sup> <sup>with</sup> <sup>an</sup> <sup>A</sup> by the etching liquid constituted of the mixed liquid of fluoric acid and nitric acid, whereby the x-ray silicon frame body 11a is formed, and the x-ray mask is thus obtained (see Fig. 3(D)). In this case, the <sup>an</sup> electron beam (EB) resist is generally used as the resist, and the pattern is formed by means of ~~the~~ EB lithography.

10 The misalignment of the x-ray absorbing film pattern of the x-ray mask manufactured by this embodiment <sup>was</sup> ~~is~~ evaluated by the coordinate measuring device. As a result, the position precision <sup>was</sup> ~~is~~ 15 nm <sup>which is</sup> ~~and~~ sufficient.

[Embodiment 3]

15 This embodiment is the same as the first and second embodiments except that the following mechanochemical polishing is performed as the step of polishing the silicon carbide film which is the x-ray membrane 12 in the step of forming the x-ray membrane 12 in the first and second embodiments.

20 The mechanochemical polishing of this embodiment is carried out in the following manner. That is, the substrate is brought into contact with <sup>a</sup> ~~the~~ solidifying polymer type abrasive cloth in which <sup>a</sup> ~~the~~ colloidal silica (its particle diameter: 60-80 nm) is dispersed, and then <sup>a</sup> ~~the~~ load of 180 g/cm<sup>2</sup> is applied to the substrate while the substrate is rotated at 60 rpm, whereby <sup>the</sup> ~~the~~ 25 substrate

surface is polished for ten minutes. At this time, 30% of H<sub>2</sub>O<sub>2</sub> is  
A added into colloidal slurry, <sup>and the</sup> <sup>the</sup> whereby pH of <sup>a</sup> solvent medium is  
A changed into <sup>a</sup> weak alkali (8.5). In such a manner, a catalytic  
A action gets active, and thus <sup>a</sup> polishing speed can be increased,  
5 A and the surface ~~can be~~ smoothed.

In this embodiment, after the polishing of the x-ray membrane is completed, the distribution of the surface roughness of the x-ray membrane is determined in the same manner as the first embodiment. As a result, the distribution is 0.12, and the 10 average of the surface roughness is 0.85 nm.

After forming the x-ray absorbing film, the stress distribution of the x-ray absorbing film is determined in the A same manner as the first embodiment. ~~As a result, the stress~~ <sup>The resulting stress</sup>  
distribution is  $0 \pm 6$  MPa.

15 Furthermore, the misalignment of the x-ray absorbing film pattern of the x-ray mask manufactured by this embodiment is A evaluated by the coordinate measuring device. ~~As a result,~~ the A position precision is 20 nm <sup>which</sup> ~~and~~ satisfies the required position precision.

20 [Comparison example]

A This comparison example is the same as the first embodiment, except the method of fixing the rear surface of the substrate on which the x-ray membrane 12 is formed to the stainless (SUS) jig in the step of polishing the x-ray membrane 12 in the above-25 A mentioned first embodiment. ~~That is, unlike~~ <sup>Unlike</sup> the first embodiment

(the water affixing method is used in the first embodiment), the  
A rear surface is fixed by the use of a wax in the comparison  
example.

In this comparison example, after the polishing of the x-ray  
5 membrane is completed, the distribution of the surface  
A roughness of the x-ray membrane is determined in the same manner  
A as the first embodiment. ~~As a result~~, the distribution is 0.25,  
and the average of the surface roughness is 0.43 nm.

After forming the x-ray absorbing film, the stress  
10 distribution of the x-ray absorbing film is determined in the  
A same manner as the first embodiment. ~~As a result~~, <sup>The resulting stress</sup>  
distribution is  $0 \pm 15$  MPa.

Furthermore, the misalignment of the x-ray absorbing film  
pattern of the x-ray mask manufactured by this embodiment is  
15 A evaluated by the coordinate measuring device. ~~As a result~~, the  
A position precision is 35 nm ~~and~~ <sup>which</sup> cannot satisfy the required  
position precision.

Fig. 4 is a table generally showing the distribution value  
of the surface roughness of the x-ray membrane, the average of  
20 the surface roughness of the x-ray membrane, the stress  
distribution of the x-ray absorbing film and the position  
precision of the x-ray absorbing film pattern of the above  
embodiments and the comparison example. Although a compound  
of Ta and B (Ta/B=8/2) is used as the x-ray absorbing film in the  
25 above-mentioned embodiments, this may be replaced by a metal Ta,

4 an amorphous material containing Ta and tantalum boride, having a composition other than Ta<sub>4</sub>B, for example.

Additionally, a structure of the x-ray mask blank is not only the structure of the embodiments but also the so-called 5 membraned structure in which the x-ray membrane is formed on the substrate and the center is then removed from the rear surface of

6 A the substrate, so as to form the frame body whereby the x-ray

7 A membrane is laminated on this frame body. ~~That is,~~ <sup>Accordingly</sup> it may safely be said that all the intermediate products in the step of 10 A manufacturing the x-ray mask are ~~the x-ray mask blank~~ <sup>blanks</sup>.

Furthermore, an adhesive layer, a reflection preventing film or the like may be disposed between the x-ray membrane and the x-ray absorbing film. In this case, after forming these films, a defect is checked on the surface thereof.

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